

APPLICATION OF CROWN ETHERS AS PHASE TRANSFER CATALYSTS
IN THE ELECTRON TRANSFER REACTIONS OF COAL

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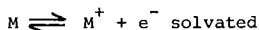
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INTRODUCTION

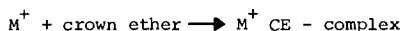
The electron transfer reactions of coal as exemplified by the Sternberg procedure (1) for reduction and reductive alkylation has been the subject of intensive investigation by a number of research groups (2-5). The reaction suffers from the problems of extended reaction time, side reactions, incorporation of the electron transfer agent and/or solvent into the coal. Further, in most cases, negligible quantities of soluble products were obtained on quenching the reaction immediately after the electron transfer step.

In view of this, the discovery by Pedersen (6,7) that certain macrocyclic polyethers called crown ethers have the ability to complex alkali metal cations, and the results of Dye (8), Kaempf (9) in the solubilization of alkali metals using these crown ethers, prompted us to envision the use of crown ethers to act as phase transfer catalyst in the electron transfer reaction with coal.

Thus, a stable solution of electrons can be prepared in an inert ethereal solvent like THF at room temperature because the equilibrium



is shifted to the right by the complexation equilibrium



The limitations of solubility, decomposition problems, reactivity and incorporation of the electron transfer agent can be overcome.

Another important facet of the crown ethers is that they have been successfully employed as reagents for direct solid-liquid phase transfer reactions (10). Thus, the problem of interphasic electron transport from solution to the aromatic substrate in coal would be solved, because the crown ether can function as a phase-transfer catalyst.

Further, the complexation of K by crown ether results in the metal cation being held inside the cavity of the crown ether and the resulting ion pair is loose. This would promote the irreversible electron transfer with bond cleavage (11).

EXPERIMENTAL

Coal: The Illinois No. 6 coal from the Burning Star No. 2 mine (courtesy of the Southern Company Services, Inc.) C-68.25%, H-5.30%, N-1.69%, S-3.62%, Ash-17.7% was used in the studies. It was demineralized, (12) extracted with Benzene:Methanol (3:1) to remove the trapped organic, and dried in vacuum at 100°C for 24 hours before use.

Reagents: The crown ether selected for study was the 18-crown-6, 1. This crown ether has a hole 2.6-3.2 Å in diameter. The electron donor alkali metal selected for the study was potassium because its ionic diameter is 2.66 Å and should, therefore, fit nicely in the crown ether hole resulting in a 1:1 complex. Using a 1:1 molar ratio of potassium to crown ether (CE), a 0.14 molar and 0.28 molar solution was prepared which was deep blue in color clearly indicating the presence of 'solvated electrons' in solution. This was reacted with different weights of coal under a blanket of nitrogen and the reaction quenched with water.

RESULTS AND DISCUSSION

Analysis: The percent g-atom of potassium consumed in the reaction of the K-CE reagent with coal was determined by measuring the difference in the volume of hydrogen evolved when the blank reagent and the reaction mixture was quenched with water after the same reaction period. To establish the accuracy of our analytical method and the validity of our reagent as an electron transfer agent, it was reacted with standard compounds and the mole of compound consumed per g-atom of potassium computed by the hydrogen evolution method. The values obtained compare favorably with those reported in literature (13) for the same compound using a different electron transfer agent and a different analytical method (Table 1).

TABLE 1

<u>Compound</u>	<u>Mol of Compound Required per g-atom of Metal</u>	<u>Literature Value</u>
Benzil	0.6	0.50
2-Butanol	1.29	1.1
Naphthalene	0.58	0.50

Effect of Electron Concentration and Time: The percent g-atom of potassium consumed in the reaction is a measure of the uptake of electrons by the coal resulting in the formation of the coal radical anion which undergoes cleavage at the ether and sulfur linkages. In the reaction of a 0.14 molar solution of K in THF with different weights of coal, the metal consumption increased with coal weight until it levelled off at the larger coal weights (Fig. 1).

One can deduce from this that for a given molar solution of metal, there is a certain concentration of electrons present which is going to be dependent on the amount of crown ether used. As the coal weight increases, the aromatic substrates available for electron transfer increases and more electrons are transferred to coal which is reflected in the amount of K consumed. This will continue till at a certain coal weight, all the available electrons get transferred. Any further increase in coal weight will still reflect the transfer of all the available electrons and the K consumed will be the same in each case. For the 0.14M solution, the minimum weight of coal required to be able to take up all the available electrons is 100 mg.

Increasing the K concentration to 0.31 molar showed a dramatic increase in the percent K consumed (Fig. 2) although the plot of percent K consumed against coal weight followed the same pattern as that obtained for the 0.14 molar solution. It is probably that at this increased electron concentration, a two electron transfer is taking place with the formation of the coal dianion and at the lower concentration, a one electron transfer occurs with the formation of the radical anion (Scheme 1).

Since complete electron transfer takes place at the 100 mg coal weight, it was selected for a time study. The K consumption increases very rapidly in the first thirty minutes and then levels off (Fig. 2). This suggests that the transfer of electrons proceeds very rapidly and is complete in thirty minutes with the electron concentration obtained from a 0.14M K/THF solution.

Solubility Studies: Based on the above studies, 1 g of coal was treated with 20 mmol of K in the THF with 20 mmol crown ether (0.2 molar in K), stirred for six hours and quenched with water. After rotaevaporating to dryness, the reacted coal was washed extensively with water to remove the K-salts and crown ether and extracted with THF. The degree of conversion was calculated as % solubility = wt of feed coal - wt of THF insoluble residue/wt of feed coal x 100. The elemental analysis and solubility of the feed coal and solubilized coal is summarized in Table 2.

TABLE 2

Sample	C	H	S	N	*THF		
					Solubility	H/C	O (By diff)
Feed Coal	74.47	4.97	3.55	1.42	5.9%	0.8	15.59
Reacted Coal (1 g Coal/ 0.2M K-THF Solution)	74.41	7.39	2.0	1.40	52.%	1.12	14.80

*Based on coal residue insoluble in THF. Thus any error in the weight due to presence of moisture crown ether, etc., would only mean more THF solubility than obtained.

¹H and ¹³C NMR Studies: The 470 MHz ¹H NMR spectrum of the solubilized coal is shown in Fig. 3, while the proton decoupled ¹³C NMR spectrum is shown in Fig. 4. The integration in the ¹H NMR shows that the ratio of H_{ar}:H_{sat} is 1:4. The broad peak around 3.4 ppm is assignable to the hydroxyl protons. The sharp resonance signals in the 1-1.6 ppm region are assigned to the R-CH₂-R grouping. These could also arise from methyl protons (CH₃-R), however, the absence of any methyl carbon resonances in the 11-22 ppm region rules out this possibility. Furthermore, the appearance of a group of signals in the 28-34 ppm region confirms the presence of methylene groups (-CH₂-) in a saturated ring system. This, in all probability, would be a saturated six-membered ring system joined to an aromatic ring system. The strong resonance signal at 69.7 ppm evidently comes from the C atom bearing the hydroxyl group (-CHOH) in the saturated ring. The aromatic ring carbons appear in the 125-145 ppm region. The 125-128 ppm signals are due to the protonated aromatic carbons and the 138-145 ppm signals due to quaternary naphthalenic type carbons.

Thus, by using a phase transfer catalyst 18-crown-6, rapid and effective electron transfer to coal has been achieved. This has resulted in the formation of coal radical anions or dianions depending on the concentration of the solvated electrons in solution (Scheme 1). These ions have undergone facile cleavage reactions (Scheme 2) resulting in depolymerization as demonstrated by the considerable increase in THF solubility from 5.9% for the starting coal to 52% for the reacted coal. The increase in the H/C ratio from 0.8 to 1.12 representing an uptake of 32H atoms per 100 C atoms is due in part to hydrogen pick-up from the capping of the cleavage coal radical or anion fragments. That this corresponds to reductive cleavage of the ether bonds in coal is supported by the presence of a large percent of hydroxyl groups in the solubilized coal as indicated by ¹H NMR. A Birch type reduction of the aromatics to hydroaromatics would account for the uptake of the remaining hydrogen atoms (Scheme 3) and is supported by the appearance of the R-CH₂-R grouping in both the ¹H and ¹³C NMR.

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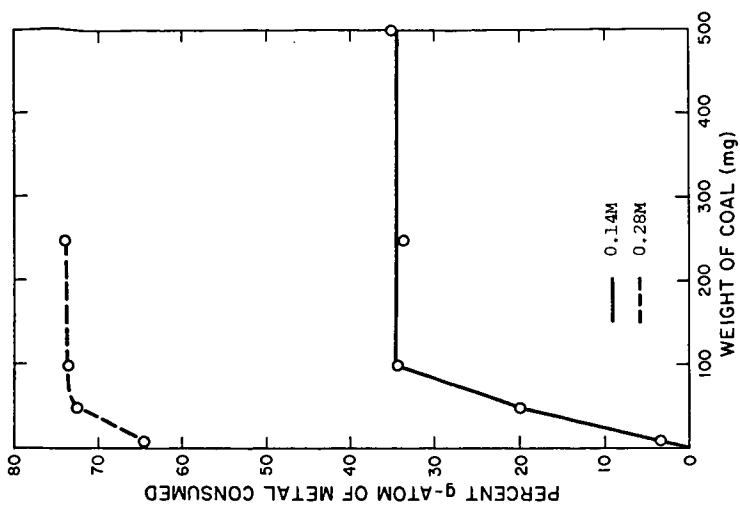


Figure 1.

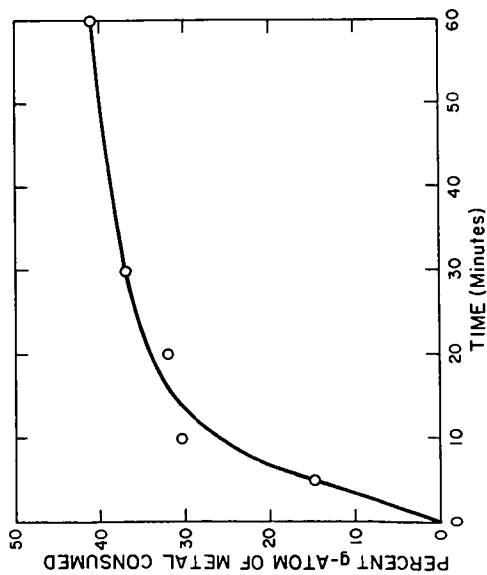


Figure 2.

Figure 3.

^1H NMR

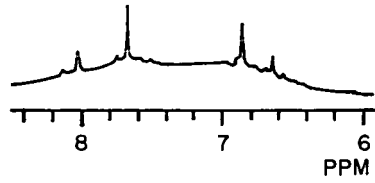
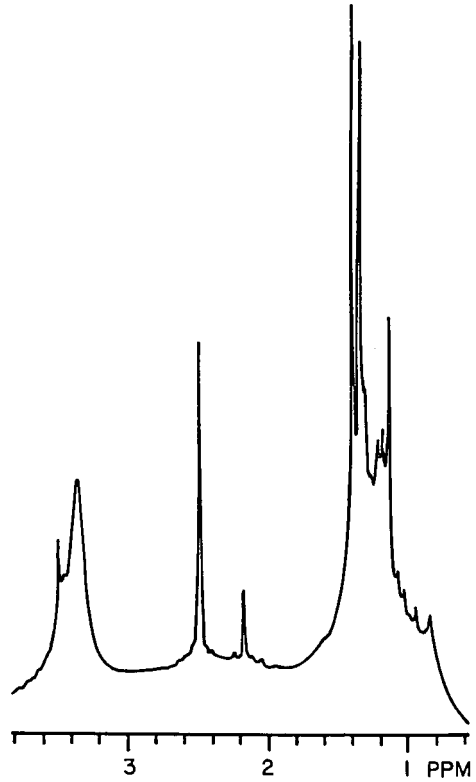
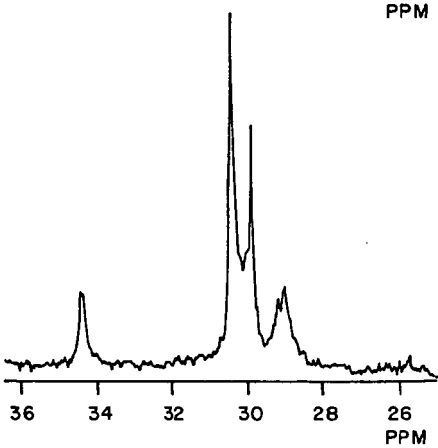
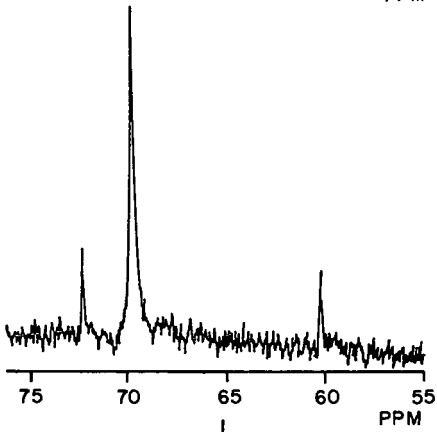
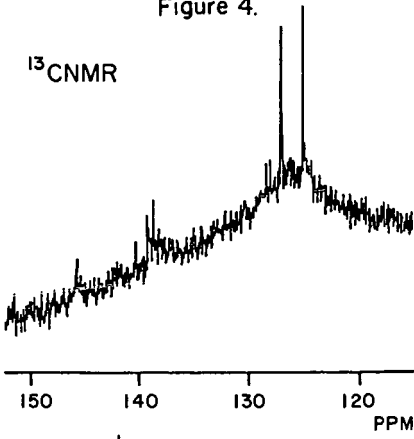
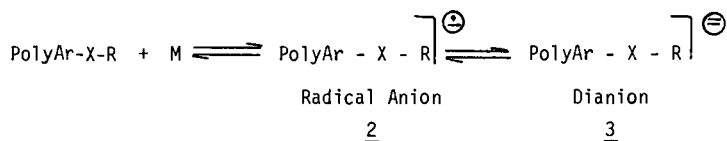


Figure 4.

^{13}C NMR

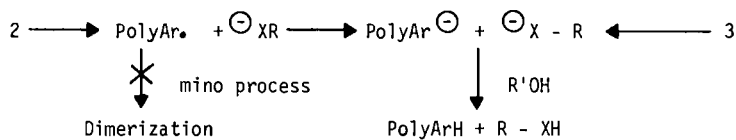


Scheme - 1



R = Aromatic, Hydroaromatic
 - CH₂Ar, -S Ar
 X = -O, S

CLEAVAGE (Scheme 2)



REDUCTION (Scheme 3)

